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DUCLAUX'S METHOD FOR THE ESTIMATION OF "VOLATILE FATTY ACIDS," THE LAWS GOVERNING "VOLATILITY" DEDUCED THEREFROM, AND THEIR APPLICATION TO ANALYSIS, MORE ESPECIALLY TO THAT OF BUTTER.

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Part I.—The Mathematical Deductions from the Distillation of Acids of the $C_nH_{2n+1}COOH$ Series.

Duclaux, from a study of the behaviour of the lower fatty acids of the series $C_nH_{2n+1}COOH$ on distillation in dilute aqueous solution, found that each acid had its own rate of distillation, whether distilled alone or mixed with its homologues, and used this as a means of estimating the members of this series. (*Ann. Chim. Phys.* [5] ii., 223.)

His experiments and method are well known, but the latter has not come largely into use; though Duclaux obtains excellent results with it, other experimenters are not successful in obtaining results comparable with his (*cf.* Allen, "Commercial Organic Analysis," i., 411; Violette, *Compt. Rend.*, cxi., 345; and Wilson, *Journ. Soc. Chem. Ind.*, ix., 18). I have from time to time used this method, and though my results are approximately in agreement with those of the originator, I have pointed out marked discrepancies (*Staz. Sper. Ag. Ital.* xxiii., 5); a recent study of the method has convinced me that Duclaux's method is vitiated by unsuitable conditions of experiment, and that his mathematical deductions from his results are erroneous.

Duclaux founds his theoretical considerations on the axiom that "the quantity of acid which vaporizes at a given moment is proportional to that which exists at the same moment in the heated liquid"; this mode of expression is unfortunate, as it is not definitely stated whether the quantity of acid existing in the liquid at a given moment is the absolute quantity, the quantity relative to the amount of liquid at that moment, or the quantity relative to the amount of liquid at the commencement of distillation; it is evident that the absolute quantity cannot be meant, and we are left with two alternatives. A little consideration shows that the quantity relative to the amount of liquid at the given moment is the correct mode of interpretation; whether 100 c.c. or 50 c.c., or any other quantity, of liquid is distilled, the vapour should have the same composition, and it is not reasonable to refer the composition of the liquid to some bulk which it had in the past. Duclaux, however, assumed the latter alternative, that the quantity of acid in the heated liquid is expressed in terms of the

bulk of liquid at the commencement; this is plainly shown by the form of equation deduced (*cf.* Wynter Blyth, "Foods," p. 450):

$$a = Y(1 - e^{-m\frac{l}{L}}).$$

That this form of equation is not correct is shown by the fact that it either requires a proportion of acid distilled before the commencement of the distillation, or more or less than 100 per cent. when the distillation is complete—an assumption which it is difficult to make, and its fallacy is borne out by the equation agreeing only with a portion of the results.

I have studied the distillation of butyric acid (*loc. cit.*), and proposed an equation of the form

$$x = Ay - By^2 + Cy^3.$$

In this I fell into an error in the mathematical deductions, *i.e.*, that both the quantity of acid distilled and the condensation in the retort were functions of the volume of the distillate, and a further study has now revealed the error.

Starting from Duclaux's axiom, it follows that the relation between the composition of the vapour given off at any moment and the composition of the liquid should be constant; this is Henry's law of the distribution of a gas between a space and a solvent. In other words, the volatile fatty acids in dilute solution may be assumed to exist as perfect gases, which is in accordance with recent theories of solution. The relation between the composition of the vapour and the composition of the liquid should be the inverse ratio of the vapour-pressure of the acid $C_nH_{2n+1}COOH$ as a perfect gas at 100° C. to the solubility of the acid in water at 100° C.; or, in other words, the rate of distillation is an inverse function of the solubility of the acid in water.

The apparent paradox pointed out by Duclaux, that the higher the molecular weight of the acid, and also boiling-point, the faster is the rate of distillation, is easily explained. For example, butyric acid boils at 162·5° C., but when a dilute aqueous solution is distilled, it passes over faster than water. We in this case measure the boiling-point of a compound $(C_3H_7COOH)_x$, but in dilute aqueous solution the compound C_3H_7COOH exists, the acids $C_nH_{2n+1}COOH$ being unknown in the pure state (*cf.* Ramsay and Shield, *Journ. Chem. Soc.*, lxviii., 1089).

The general equation that I have deduced from the results obtained by Duclaux (and in the case of butyric acid by Wollny and myself) is

$$(100 - y) = \frac{(100 - x)^a}{100^{a-1}} \times K^{-x}.$$

x = percentage volume distilled.

y = percentage of acid distilled.

The expression K^{-x} is, as I shall show, an approximation to the condensation in the retort, and may be neglected here. The expression then stands

$$100 - y = \frac{(100 - x)^a}{100^{a-1}}. \quad . \quad . \quad . \quad (1).$$

The quantity of acid existing in the retort at any moment is

$$\frac{100 - y}{100 - x} = \frac{\frac{(100 - x)^a}{100^{a-1}}}{100 - x} = \frac{(100 - x)^{a-1}}{100^{a-1}}. \quad . \quad . \quad . \quad (2).$$

The quantity of acid vaporizing at that moment is the first differential coefficient of

$$(1) = a\frac{(100 - x)^{a-1}}{100^{a-1}}. \quad . \quad . \quad . \quad (3).$$

The ratio of the composition of the vapour to that of the liquid is the ratio of (2) to (3), that is, a, which shows that equation (1) fulfils Duclaux's axiom, and also Henry's law. The effect of condensation in the retort is of importance, as it follows from Henry's law that the composition of the condensed liquid will not be the same as that of the vapour; if a is greater than 1, the condensed liquid will be weaker than the vapour, and if less, stronger; if a is greater than 1, the condensed liquid will also be stronger than the liquid in the retort, and if a is less, weaker. The effect of this being cumulative, a considerable deviation from equation (1) may be noticed. The loss by condensation is of course a function of the composition of the vapour, and I have expressed it as a logarithmic function of the volume of the distillate. Owing to the condensation being small, the composition of the vapour may be assumed, without great error, to bear an approximately constant proportion to its bulk, and my expression K^{-x}, though not really correct, is a sufficiently close approximation; of course, this correction is only applicable if the perfect gaseous state is assumed, and where it is not may disappear, and the value of the sign may even be reversed.

There is also a loss by imperfect condensation, unless special precautions are taken, and when a exceeds 1, this loss may make a noticeable difference; thus I have found a loss of 2 per cent. of the total amount of butyric acid on distilling a dilute solution, when the total loss of liquid by imperfect condensation has been 0·4 per cent. I have assumed that this loss is directly proportional to the acid distilled, and have eliminated the source of error by taking the total amount of acid to be the sum of the distillate, and that remaining in the retort and condenser; I have corrected some of Duclaux's series on this account.

The corrections on account of condensation being small, the error of these will lie within the limits of experimental error.

The following values of a and K in the general equation

$$100 - y = \frac{(100 - x)^a}{100^{a-1}} \times K^{-x}.$$

	a.	K.
Formic acid (Duclaux)	0·4	1·00079
Acetic ,, ,, ...	0·667	1·
Propionic acid (Duclaux)	1·111	1·000723
Butyric ,, ,, ...	2	1·
,, ,, (Wollny)	2	1· (?)*
,, ,, (Richmond)	2	1·0023451
Valeric ,, (Duclaux)...	3	1· (?)
Caproic ,, ,, ...	4	1·003508
Caprylic ,, ,, ...	8 (?)	(?)

In the following tables are given the experimental results and the calculated values. Column I. contains the percentage volume of the distillate; Column II. the percentage of acid distilled; Column II.a the corrected values of this (when neces-

* K in this case is probably not constant, as W. used a 5 per cent. solution, and it is probable that the perfect gaseous state was not attained.

sary); Column III. the calculated values of y; Column IV. the difference; Column V. the strength of the liquid in the retort; Column VI. the strength of the vapour given off; and Column VII. the ratio between them.

FORMIC ACID.

I. x	II. y	III. y (calc.)	IV. diff.	V.	VI.	VII. a
9·09	3·5	3·5	—	106·2	41·2	·39
18·18	7·6	7·3	− ·3	113·3	45·1	·40
27·27	11·8	11·5	− ·3	121·3	47·3	·39
36·36	16·3	16·1	− ·2	131·5	52·8	·40
45·45	21·6	21·1	− ·5	143·7	60·5	·42
54·54	27·3	26·8	− ·5	160·0	66·0	·41
63·63	33·7	33·3	− ·4	182·3	77·0	·42
72·72	41·4	41·0	− ·4	214·9	92·7	·43
81·81	50·7	50·5	− ·2	271·4	118·5	·44
90·9	63·5	63·5	—	401·5	208·5	·5

ACETIC ACID.

I.	II.	III.	IV.	V.	VI.	VII.
9·09	5·9	6·2	+ ·3	103·5	67·1	·65
18·18	12·2	12·5	+ ·3	107·3	70·5	·66
27·27	18·8	19·1	+ ·3	111·7	73·7	·66
36·36	25·6	26·0	+ ·4	117·0	77·2	·66
45·45	32·7	33·3	+ ·4	123·1	81·5	·66
54·54	40·5	40·8	+ ·3	131·6	86·7	·66
63·63	48·7	49·0	+ ·3	140·9	95·2	·67
72·72	57·9	57·9	—	154·2	104·5	·68
81·81	67·7	67·9	+ ·2	177·5	119·3	·67
90·90	79·8	79·8	—	222·2	166·5	·75

PROPIONIC ACID.

I.	II.	III.	IV.	V.	VI.	VII.
9·09	10·5	10·6	+ ·1	98·5	116·0	1·18
18·18	21·1	21·0	− ·1	96·4	115·5	1·20
27·27	31·5	31·2	− ·3	94·2	111·6	1·18
36·36	41·4	41·1	− ·3	92·2	108·9	1·18
45·45	51·3	50·7	− ·6	89·0	105·6	1·18
54·54	60·6	59·9	− ·7	86·6	100·1	1·16
63·63	69·5	68·9	− ·6	86·5	95·7	1·11
72·72	78·0	77·6	− ·4	80·6	90·0	1·12
81·81	85·8	85·8	—	77·8	81·4	1·05
90·90	92·8	93·5	− ·7	79·0	79·1	1·0

BUTRYIC ACID (WOLLNY).

I.	II.	III.	IV.	V.	VI.	VII.
10	18·2	19·0	+ ·8	90·9	176·6	1·94
20	35·3	36·0	+ ·7	80·9	161·7	2·00
30	50·4	51·0	+ ·6	70·9	140·3	1·98
40	63·6	64·0	+ ·4	60·7	121·0	1·99
50	74·9	75·0	+ ·1	50·2	104·0	2·07
60	84·2	84·0	− ·2	39·5	82·5	2·09
70	91·1	91·0	− ·1	29·7	62·0	2·09
80	96·3	96·0	− ·3	18·5	40·0	2·16

BUTYRIC ACID (DUCLAUX).

I.	II.	IIa.	III.	IV.	V.	VI.	VII.
9·09	17·1	17·4	17·4	—	90·9	184·2	2·03
18·18	32·7	33·4	33·1	− ·3	81·4	164·1	2·02
27·27	46·3	47·1	47·1	—	72·7	144·1	1·98
36·36	58·5	59·5	59·5	—	63·6	126·5	1·99
45·45	68·8	70·0	70·3	+ ·3	55·0	106·7	1·94
54·54	77·5	78·8	79·3	+ ·5	46·6	88·0	1·89
63·63	84·3	85·9	86·7	+ ·8	38·8	72·6	1·87
72·72	90·2	91·8	92·5	+ ·7	30·7	58·3	1·90
81·81	94·6	96·3	96·7	+ ·4	20·4	43·3	2·12
90·90	97·5	99·2	99·2	—	8·9	28·6	3·2

BUTYRIC ACID (RICHMOND).

I.	II.	III.	IV.	V.	VI.	VII.
9·09	19·1	19·1	—	89·0	195·9	2·20
18·18	35·4	35·1	− ·3	78·6	170·5	2·18
27·36	50·0	50·5	+ ·5	68·8	150·4	2·18
36·45	62·6	62·8	+ ·2	58·9	127·6	2·17
45·73	73·1	73·1	—	49·6	103·6	2·09
54·82	81·3	81·5	+ ·2	41·4	85·0	2·05
64·09	88·5	88·5	—	32·0	70·2	2·19
73·18	93·7	93·7	—	23·5	50·0	2·13
81·90	97·4	97·2	− ·2	14·3	34·1	2·4
91·45	99·3	99·4	+ ·1	8·2	17·6	2·15

VALERIC ACID.

I.	II.	IIa.	III.	IV.	V.	VI.	VII.
9·09	24·5	25·2	24·9	− ·3	82·3	254·6	3·09
18·18	44·5	45·8	45·3	− ·5	66·2	202·4	3·06
27·27	59·5	61·3	61·6	+ ·3	53·2	152·9	2·87
36·36	71·3	73·2	74·3	+ 1·1	42·1	111·4	2·65
45·45	79·5	81·9	83·8	+ 1·9	33·2	84·7	2·6
54·54	85·7	88·3	90·6	+ 2·3	25·7	59·4	2·3
63·63	89·7	92·4	95·2	+ 2·8	20·9	42·1	2·0
72·72	92·8	95·6	98·0	+ 2·4	16·1	33·0	2·1
81·81	95·4	98·3	99·4	+ 1·1	9·3	25·0	2·7
90·90	96·9	99·9	99·9	—	?	?	?

CAPROIC ACID.

I.	II.	III.	IV.	V.	VI.	VII.
9·09	33·5	33·9	+ ·4	73·2	320·1	4·4
18·18	56·0	58·0	+ 2·0	53·8	232·2	4·3
27·27	75·5	74·5	− 1·0	33·7	179·9	5·3
36·36	86·0	85·6	− ·4	21·7	98·0	4·5
45·45	92·5	92·5	—	13·7	61·0	4·5
54·54	96·5	96·5	—	7·7	37·4	4·9
63·63	97·5	98·6	+ 1·1	6·8	10·5	1·5
72·72	98·4	99·6	+ 1·2	5·9	9·9	1·7
81·81	99·3	99·9	+ ·6	3·8	8·8	2·3
90·90	100·0	100·0	—	?	?	?

Duclaux's figures for caprylic acid do not agree very well with a formula of the type given above, but the approximate value of a is 8.

The agreement, except in the case of valeric acid, is, considering the nature of the experimental error, good. The three series for butyric acid are interesting, as Wollny used a 5 per cent. solution, Duclaux a 1 per cent. solution, while mine was of about 0·3 per cent. strength, and though the different effect of condensation is plainly shown, yet our results all lead to the same value for the rate of distillation.

The figures in Column VI. for the strength of the vapour are obtained by interpolation, and from the quantities distilled; they do not, however, strictly represent the composition of the vapour in the retort, as not only is the condensation in the retort affecting this result, but a small error will be introduced during the condensation in the condenser, the condensed liquid not having exactly the same composition as the vapour; after allowing for this, and for the error in calculating the figures in Column VI., we see that the figures in Column VII. are approximately constant, and are nearly of the value of a in the formula.

It is evident that though a is constant for each acid, K will depend on the conditions of work, and this explains why other experimenters do not obtain results comparable with those of Duclaux. I am engaged in making experiments with an apparatus modelled on that of Brown (*Journ. Chem. Soc.*, xxxix. 304), and thus hope to eliminate the function K^{-a}.

The following laws of the volatility of the acids $C_nH_{2n+1}COOH$ may be laid down:

(i.) Each acid of the series $C_nH_{2n+1}COOH$ on distillation in dilute solution behaves as a perfect gas and conforms to Henry's law.

(ii.) Each acid has a fixed rate of distillation, which is an inverse function of its solubility in water, and is quite independent of the properties of the pure acids.

(iii.) The apparent rate of distillation may be modified by condensation in the retort.

(*To be continued.*)

Ang-Khak, a Chinese Dye used for the Coloration of Articles of Food, etc. H. C. Prinsen. (*Chem. Zeit.*, 1895, xix., 1311.)—Ang-khak is a purple-coloured substance formed by the action of a particular ferment on cooked rice, but the exact method of its preparation is unknown. In order to detect its presence in red wine, the liquid should be shaken with chloroform; if the latter remain colourless, ang-khak is absent. In the event of any red colour being extracted, a large quantity of the wine should be evaporated to dryness with sand, extracted with chloroform, and examined. It may be distinguished from any of the aniline colours by being precipitated by mercuric oxide, and by some other colour-reactions, which are indicated in the table. A is a pure red wine, C a 10 per cent. solution of ang-khak in alcohol, and B a mixture of four parts of wine and one of C.

	A.	B.	C.
1 c.c. wine + 4 c.c. soda (1 : 200)	Greenish.	Greenish-brown.	Red.
1 c.c. wine + 3 c.c. NH_3 (1 : 100) + 5 c.c. water	,,	Brown.	Red.
4 c.c. wine + 1 c.c. alum (1 : 10) + 1 c.c. soda (1 : 10) filtered — filtrate	Colourless.	Red.	,,
4 c.c. wine + 1 c.c. alum (1 : 10) + 1 c.c. soda (1 : 10) filtered — ppt.	Gray.	Violet.	,,
2 c.c. wine + 1 c.c. lead acetate — filtrate	Colourless.	Red.	,,
2 c.c. wine + 1 c.c. lead acetate — ppt. ...	Gray.	Violet.	,,
10 c.c. wine + 0·5 grm. HgO—filtrate ...	Colourless.	Colourless.	Colourless.
5 c.c. wine + 2 c.c. chloroform, the chloroform is	Colourless.	Red.	Red.

F. H. L.

Some Samples of Italian Butter. P. Spallanzani and A. Pizzi. (*Staz. Sper. Ag. Ital.*, xxxviii., 257.)—Fortnightly analyses of butters from six localities in the province of Reggio, and of a few from the provinces of Modena and Parma, were made for the twelve months, March, 1894, to February, 1895. The Reichert-Wollny method was used without modification for the determination of the volatile acids, and the density of most of the samples and the refractive index of a few were also determined. One of the six localities chosen was the dairy attached to the Dairy School of Reggio, and the butters were prepared in the other five localities under the continued supervision of trustworthy and competent persons, and came from dairies where the care and good faith of the proprietors were considered above suspicion.

The lowest Reichert-Wollny figure obtained was 19·80 c.c., and the highest 30·14 c.c.; the density at 100° C. varied from 0·8640 to 0·8680, and the refractive index, measured with Zeiss' butyro-refractometer at 35° C., from 47·2 to 43·5.

The authors note that of the butters manufactured at the Dairy School at Reggio but two were below 25 c.c. (viz., 24·64 and 24·53), while in the other five localities butters giving below this figure were almost universal in November, December, January, and February. In all parts it was found that during the months of May, June, July, and August the Reichert-Wollny figure was uniformly high. The butters which gave low Reichert-Wollny figures were obtained when the yield was very small, and consequently, although the numeric mean was found to be 25·84 c.c., the average taking quantities produced into account was over 28 c.c., a normal figure.

The authors discuss the influence of feeding, and show that when the cows are out to grass the butter is rich in volatile acids, and when they are stall-fed, and on a poor ration, the Reichert-Wollny figure is low. They also show that higher figures are yielded in the early stages of lactation than in the later stages. A newly-calved cow yielded butter of Reichert-Wollny 28·05, while one which was at the end of its period of lactation yielded butter of Reichert-Wollny 21·23 c.c., the breed, feeding, and other conditions being the same in both cases.

They are of opinion that the larger globules of fat in milk are richer than the smaller ones, though they offer no experimental evidence of this (for an experiment showing that the large and small globules have the same composition, see Analyst, xix. 76), and from this conclude that the mode of butter-making adopted may have an influence on the composition.

They conclude that (i.) butters with a greater refractive index at 35° than 48°, and a lower density at 100° than 0·8640, can be declared adulterated.

(ii.) A Reichert-Wollny figure of less than 20 c.c. shows the presence of foreign fat; figures higher than 20 and less than 26 c.c. in May to September, and less than 23 c.c. in the other months, are suspicious (in Emilia), and appeal to the cow should be resorted to. H. D. R.

The Detection of Watered Milk by the Examination of the Milk Serum. Dr. Lescœur. (*Congres Intern. de Chim. Appliq., Comp. Rend., Brussels*, 1894, pp. 60-62.)—A means of distinguishing between a watered milk and one from which cream has been abstracted is furnished by examination of the milk serum. Coagulation of the milk is readily brought about by adding a trace of rennet, and the serum is separated by filtration.

The density of milk serum thus obtained varies from 1·029 to 1·031 at 15°. In certain samples it has been found as low as 1·027, and this the author takes as his minimum limit.

The extract of the serum should also be determined. The weight varies from 67 to 71 grammes per litre, the mean being 70 grammes and the minimum 67 grammes.

Every sample therefore which yields a serum with a density lower than 1·027, and the extract of which does not reach 67 grammes per litre, should be looked upon as watered.

The following figures show the effect of added water on the serum of a pure milk:

	Density of Serum at 15°.	Proportion of Extract per litre of Serum.
Pure milk	1·030 ...	70 grammes
,, + 10 % water ...	1·0275 ...	64 ,,
,, + 20 ,, ...	1·0251 ...	59 ,,
,, + 30 ,, ...	1·023 ...	54·5 ,,

From this it appears that the addition of about 4 per cent. of water lowers the specific gravity by one-thousandth and the weight of the extract by two units.

In milk which has curdled naturally, the serum, in spite of its different composition, gives almost the same results as does the neutral serum prepared by rennet. Hence no modification of the method is necessary for curdled milk. C. A. M.

The Chemical Variations of Different Kinds of Mace. E. Späth. (*Forschungsber. Lebensmittel. Hyg., etc.*, 1895, ii., 148; through *Chem. Zeit. Rep.*, 1895, 202.)—Banda mace may be distinguished from its usual adulterant, Bombay mace, by its containing about ten times as much essential oil. On the other hand, the latter contains more (56 per cent.) fat than the former (21 per cent.). The author has extracted this fat from a number of samples of mace from different sources by means of petroleum spirit and determined its constants. The figures obtained from mace from Banda, Menado, Penang, Macassar, and Zanzibar closely

agree with one another, being as follows: Melting-point in open tube, 25° to 26°; saponification number, 169·9 to 173; iodine number, 75·6 to 80·8; Meissl's number (for Banda only), 4·1 to 4·2; value in Zeiss's refractometer at 40°, 76 to 85; and coefficient of refraction, 1·480 to 1·487. Bombay mace gives the following: Melting-point, 31° to 31·5°; saponification number, 189·4 to 191·4; iodine number, 50·4 to 53·5; Meissl's number, 1·0 to 1·1; Zeiss, 48 to 49; coefficient of refraction, 1·463 to 1·464. The fat of mace "scales, *i.e.*, the covering inside the seed mantle," differs considerably from that of the arillus itself, especially in melting-point (28·5° to 29°) and in saponification number (148·2 to 148·8); its iodine number is also low (71·3 to 73·4). F. H. L.

On the Isolation, Quantitative Separation, and Chemical Characteristics of Alkaloids and Glucosidal Bodies in Forensic Cases. Carl Kippenberger. (*Zeit. f. anal. Chem.*, 1895 [3], pp. 294-346.) — The investigations of the author have been made with special reference to the detection of poisonous alkaloids in the dead body. The products of the decomposition of animal cells after death, which in certain cases give with tannic acid, iodine, and other reagents reactions simulating those of alkaloids, have hitherto been among the chief difficulties in the examination. While many have studied the reactions of these cadaveric "alkaloids," but little work has been done to determine their chemical constitution, and in isolating them too little care has been taken to ensure that albumin and its further decomposition products have been absent. In the author's opinion, which is based on experiment, the reactions obtained with the so-called cadaveric alkaloids are in many cases due to the presence of albuminoid compounds, and there is good reason to doubt whether among the normal decomposition products of the dead body any substances occur which are completely analogous in chemical composition to the vegetable alkaloids.

It is of the greatest importance, therefore, to remove peptone and albumin from the extract, and this may be most readily done by precipitation with tannic acid, no trace of them being then found in the filtrate. Most alkaloids are also precipitated with tannic acid, but these alkaloidal compounds are soluble in fluids containing glycerin, and may thus be separated in a pure state. The author's experiments on extracting parts of the decomposed body with and without the addition of vegetable alkaloids completely confirm the value of this means of separation. The action of the glycerin on the compounds of the alkaloids and tannic acid is not merely that of a solvent, for it is shown that a definite compound is formed with them.

For removing the alkaloids from the extracted fluid, chloroform gives better results than ether as used in the Stas-Otto method. It does not take up water from the aqueous solution, is a much better solvent for many glucosidal bodies, and gives a more quantitative removal, especially with strychnine and atropine. The glycerin separates well from the chloroform when the latter is present in at least equal volume. The best solvent for removing fat is petroleum spirit with a boiling-point of from 30° to 35° C. It separates readily, and does not dissolve in the glycerin.

The alkaloids, morphine, narceine, curarine, and the poisonous substance strophantin, will not go into solution in chloroform, ether, etc., either from acid or alkaline (fixed alkalies) solution. With the exception of curarine they dissolve, how-

ever, when shaken up with ammonia solution, with the addition of a little warm amyl alcohol. The drawback to this is the impurities contained in the amyl alcohol.

Saturation of the solution with common salt offers a means of separating many alkaloids from aqueous solution, and they may then be taken up by a solvent which does not mix with the salt solution.

Further experiments showed that morphine is precipitated by alkaline carbonates, and that narceine, while not so insoluble, is still rendered capable of being shaken out with chloroform containing some alcohol. If, then, in the second stage of shaking out, alkaline bicarbonate be added to the liquid made alkaline with alkaline hydroxide, morphine and narceine are removed by shaking with chloroform containing 10 per cent. of alcohol. The alkaloids may be recovered from the separated chloroform by shaking with acidified water.

Strophantin remains most stubbornly in the aqueous solution, but may be separated by means of a mixture of equal parts of chloroform and ether, in which it dissolves after being shaken both in acid and alkaline solution.

The general method of procedure used by the author is as follows:

1. The animal matter to be examined for poisons is extracted for two days at about 40° C., with glycerin containing a large amount of tannic acid in solution, with or without the addition of water. The fluid, after the solid matter has been removed, is freed from blood fibrin and dissolved albumin* by heating to about 50° C. and filtering after cooling.

2. Fat is removed by shaking up twice with petroleum spirit, the last traces of the latter being removed by heating on the water-bath. The alkaloids are then shaken out with chloroform (*a*) from acid solution, (*b*) from alkaline solution, (*c*) from alkaline bicarbonate solution. Finally, the fluid is shaken with a mixture of chloroform and ether after saturation with common salt.

The treatment with petroleum spirit removes traces of veratroidine and jervine, besides the fat. On shaking the acidified liquid with chloroform, the following alkaloids are removed: Colchicine, digitaline, picrotoxine, cantharidine, papaverine, aconitine, narcotine, jervine, geissospermine, small quantities of delphinine, brucine, and veratrine, with traces of narceine and strychnine.

The fluid made alkaline with alkaline hydroxide and shaken with chloroform yields atropine, codeine, emetine, brucine, veratrine, sparteine, coniine, nicotine, strychnine, pilocarpine, apomorphine, and any narcotine and papaverine left from the previous shaking. Chloroform removes from the solution, after the addition of alkaline bicarbonate, morphine and narceine, while strophantin is extracted as described above.

Instead of direct extraction with the glycerin tannic acid solution, the extract may be first obtained by the usual Stas-Otto method, and then subjected to the method of treatment proposed by the author. This has, however, the disadvantage that certain inorganic poisons if present dissolve in the glycerin, and a more tedious process will be necessary to detect them.

* "vom Blutfibrin und eventuell gelösten Albumin durch Erhitzen auf circa 50° C. befreit."

Estimation, Separation, and Chemical Characteristics of Alkaloids and Glucoside Bodies.

A. Methods for the Estimation of Single Alkaloids.

The estimation of an alkaloid when present in the pure state is readily carried out by controlling the gravimetric results by titration with acid. In forensic cases this cannot as a rule be done, owing to the chloroform taking up traces of acid and alkali during the shaking out. The gravimetric determination must therefore be controlled by a titration method applicable to acid and neutral solutions of the alkaloid. For this purpose solutions of iodine or mercuric iodide in potassium iodide are suitable; also, in special cases, a solution of mercuric chloride.

Iodine Solution.—R. Wagner (*Journ.*, 1861, p. 867) proposed precipitating the alkaloid in solution with excess of iodine, and titrating back with thiosulphate. Schweissinger (*Arch. d. Pharm.*, 1885, 615) showed that the presence of mineral acids did not affect the result, but that the alkaloid compound gradually decomposed on contact with water, and to obviate this he recommended filtering rapidly under pressure and titrating the excess of iodine in the filtrate. The author proves that this method, if carried out under certain precautions, gives results corresponding closely to those required by theory: A measured volume of the alkaloid solution is placed in a glass-stoppered flask and diluted with a measured volume of water. Iodine solution ($\frac{1}{20}$ N) is then added till no further precipitate forms, and the liquid well shaken. After standing from five to ten or fifteen minutes, according to the character of the alkaloid, it is filtered through asbestos, and the excess of iodine determined with $\frac{1}{20}$ N thiosulphate solution in an aliquot part of the filtrate. All the alkaloids tried gave good results with the exception of brucine. This is explained by the author on the supposition that the brucine compound is more readily decomposed by water, and that, in addition to the compound Alk. $HI.I_2$ of the alkaloids in general, the compound Brn. HI.I is also formed.

In titrating morphine salts, the presence of acid (HCl) and of NH_4Cl exercises a solvent action. With the other alkaloids they do not interfere, but rather promote the separation.

As a general rule, titration of the alkaloids with iodine solution is to be recommended except in the case of brucine.

Mercuric Iodide in Potassium Iodide Solution (*Mayer's Reagent*).—This gives with most alkaline solutions an insoluble precipitate, on which fact a titration method is based. The solution contains 13·546 grammes $HgCl_2$ and 49·8 grammes KI per litre. The 13·546 grammes $HgCl_2$ correspond to 12·69 grammes I, from which the amount of alkaloid is calculated. The method gives useful results, but too large an excess of KI must be avoided. The author points out that 1 c.c. of the solution does not correspond to 0·0213 gramme of narcotine, as given in the text-books, but to 0·02065 gramme.

Mercuric Chloride Solution.—The author has experimented with mercuric chloride solution, which in many cases gives an insoluble precipitate with alkaloids. Although in certain cases good results may be obtained, the number of alkaloids

with which the method can be used is limited, and there is no superiority over titration with iodine solution.

B. Separation of Mixtures of Alkaloids, and Chemical Characteristics of Individual Alkaloids and Glucosides.

1. *Alkaloids and Glucosides removed by Chloroform from Acid Solution.*—From the acidified tannic acid solution there separate the tannin compounds of colchicine, digitalin, papaverine, narcotine, delphinine, aconitine and agaricine, while picrotoxin and cantharidin remain in solution.

Of these the following are soluble in water made alkaline with alkaline hydroxide: Cantharidin and picrotoxin, agaricine, colchicine and digitaline, while delphinine, aconitine, narcotine and papaverine are insoluble.

By "acidified tannic acid solution" the author means his separation-reagent described above, to which HCl or H_2SO_4 has been added to turbidity, and then water until it just becomes clear again.

Separation of Aconitine, Narcotine, and Papaverine.—The picrates are formed by decomposing the alkaloid salts with an aqueous solution of picric acid. While wet the insoluble picrates are washed with ammonia solution. Narcotine and papaverine dissolve, while aconitine is left. The solution must not be too dilute since aconitine picrate is slightly soluble in water. With rapid filtration accurate results may be obtained.

Separation of Narcotine and Papaverine.—This is best effected in the form of oxalates. The di-oxalate of papaverine is almost insoluble in cold alcohol and in water, while the corresponding compound of narcotine is readily soluble.

Potassium ferricyanide precipitates papaverine from its neutral solutions. After standing twenty-four hours the separation is quantitative. The analogous compound of narcotine is difficultly soluble, but the separation is not quantitative. With delphinine and aconitine there is no precipitation.

Potassium ferrocyanide gives a precipitate with papaverine, and a similar one with narcotine, but in neither case is it quantitative. With delphinine it forms a blue precipitate.

With sodium nitroprusside papaverine forms a compound somewhat soluble in pure water and readily so in HCl. The compound with narcotine is almost insoluble in pure water, but is fairly soluble in acidified water, and readily soluble in alcohol and acetone. With delphinine the reagent forms a white precipitate, which becomes red on treatment with concentrated H_2SO_4, and dissolves in excess of nitric acid, forming a yellow solution.

Colchicine.—A characteristic reaction is the orange colour which appears on adding hydroxylamine hydrochloride followed by a slight excess of NaOH. Strong HNO_3 gives a brown colour with the alkaloid, especially on warming; on diluting and adding NaOH, this becomes orange red.

Delphinine.—This has only the reaction with tannic acid in common with digitalin, while it differs from picrotoxin in its entire behaviour. It may be readily separated from the latter by treatment with alkaline hydroxide, in which picrotoxin is readily soluble. With concentrated H_2SO_4 delphinine gives a brownish solution

resembling that given with digitalin. The reaction with potassium ferrocyanide is also very distinctive.

Cantharidin is not an alkaloid, but an acid anhydride. It is more soluble in chloroform than in ether and benzene. No new reactions are given.

Papaverine.—A most characteristic reaction is the behaviour of its chromic acid compound with H_2SO_4, a solution being formed in which, on shaking, violet stripes momentarily appear. Potassium bichromate gives a reddish-yellow precipitate with papaverine solutions. On adding H_2SO_4 to this on a tile, a green solution is formed, which gradually becomes brown.

Aconitine.—No alteration appears in the solution on adding potassium ferrocyanide, monochromates or bichromates, copper sulphate, Fehling's solution or lead acetate.

Agaricine.—A yellow powder, insoluble in acids, easily soluble in alkaline hydroxide. The tannic acid compound is readily soluble in excess of tannic acid. It slightly reduces Fehling's solution, but gives no characteristic reactions with H_2SO_4, HNO_3, or chromic acid compounds.

2. *Alkaloids removed by Chloroform from Solutions made Alkaline with Alkaline Hydroxide.*—The tannin compounds of the following are insoluble in acidified tannic acid solution: Brucine, strychnine, emetine, veratrine, narcotine, codeine and thebaine.

The analogous compounds of atropine, sparteine and nicotine are soluble.

Further Separations.—Any aconitine, papaverine, or narcotine still left in the solution can be removed by acidifying and shaking out with chloroform.

Nicotine, coniine and sparteine are liquid and volatile, and may be separated from the other alkaloids, including atropine, by distillation.

Brucine and Strychnine.—The most suitable method of separation is based on that of Dunstan and Short,* which depends on the fact that potassium ferrocyanide precipitates strychnine from acid solution, while the analogous brucine compound is soluble. The precipitate is decomposed with ammonia, the base removed by chloroform, dried at 105°, and weighed.

This was modified by Beckurts and Holst,† who added a standard ferrocyanide solution until all the strychnine was precipitated, iron chloride paper being used as the indicator.

The author has obtained accurate results by adding the ferrocyanide in slight excess, as shown by an indicator, allowing to stand for fifteen minutes, washing the precipitate as rapidly as possible, decomposing with ammonia, shaking out with $CHCl_3$, and titrating the solution with $\frac{1}{20}$ N iodine solution.

Gerock's‡ method of separating brucine and strychnine as picrates also gives useful results, but is not so good as the ferrocyanide method. Since no insoluble compound with potassium ferrocyanide is formed by atropine, codeine, emetine, veratrine, narceine or sparteine, this reagent can be used for the separation of strychnine from these alkaloids.

Separation of Brucine from Veratrine, Codeine, and Emetine.—Otto§ gives a

* *Pharm. Journ. and Trans.*, iii., 694.
† *Pharm. Centralhalle*, 1887, p. 119.
‡ *Arch. d. Pharm.*, 1889, p. 159.
§ *Anleit. zur Ausmitt. der Gifte*, 6 Edit., p. 67.

method for separating strychnine and brucine which depends on the solubility of the chromic acid compound of brucine in dilute acetic acid of sufficient concentration. But the author finds that the brucine compound is deposited after standing twenty-four hours. It is a yellow crystalline substance, and, according to the analysis, has the formula $(C_{23}H_{26}N_2O_4)_2K_2CrO_4$. On this fact he has based a separation method.

The alkaloids are dissolved in as little water as possible, neutralized with alkaline hydroxide, and the solution made feebly acid with acetic acid. A definite volume of H_2CrO_4 solution is added (9·725 grammes per litre), the liquid well shaken, and allowed to stand in a stoppered flask for twenty-four to thirty-six hours. The excess of chromate is then determined in an aliquot part of the filtrate by adding KI and HCl in excess and rapidly titrating the liberated iodine before the somewhat insoluble compounds of iodine with veratrine, codeine, or emetine have been formed.

The brucine chromate may also be estimated gravimetrically by washing with alcohol and ether and drying until the weight is constant.

With potassium bichromate brucine gives a dark-yellow precipitate, which is practically insoluble in dilute acetic acid. Veratrine only gives a precipitate in concentrated solution, and this gradually dissolves on adding excess of acetic acid. With codeine, emetine, and atropine there is no precipitate with bichromate, either in neutral or acid solution.

Brucine and Thebaine.—These can be separated by precipitation with bichromate from strongly acid solution, brucine bichromate being but little soluble under these conditions.

Brucine, Veratrine, and Thebaine.—The alkaloids are dissolved in alcohol, and a solution of mercuric chloride in alcohol added. After standing from twenty-four to thirty-six hours, the brucine compound is precipitated, while those of veratrine and thebaine remain in solution.

The behaviour of the picrates of these alkaloids towards ammonia solution is another means of separation. Brucine picrate is insoluble in ammonia solution, veratrine picrate somewhat soluble, while strychnine picrate is fairly soluble, and the picrates of atropine, codeine, and thebaine readily so.

Thebaine from Codeine and Strychnine.—The picrate of thebaine is insoluble in water containing acetic acid, while the other two are soluble.

Neither potassium ferrocyanide nor ferricyanide gives any precipitates with atropine, brucine, codeine, veratrine, emetine, and sparteine. Thebaine is precipitated by potassium ferricyanide, but not quantitatively. The compound is readily soluble in HCl.

Sodium nitroprusside at first gives no precipitate with brucine and strychnine; gradually one is deposited, but the compound is soluble in pure water and fairly soluble in acidified water.

With veratrine there is an immediate precipitate, but this is not quantitative.

3. *Alkaloids, etc., not removed by Chloroform from Acid or Alkaline Hydroxide Solution.*—Morphine and narceine are removed by $CHCl_3$ containing alcohol, and strophantin by a mixture of $CHCl_3$ and ether.

Narceine and strophantin are insoluble in acidified tannic acid solution, while morphine remains in solution.

Further Methods of Separating Morphine and Narceine.—The compounds of morphine with picric acid and iodine are soluble in ammonium chloride solution, while the analogous compounds of narceine only dissolve in traces. Quantitative results are obtained by titrating the narceine by the iodine method described above under "Estimation of Alkaloids." The ammonium chloride exercises no influence on the iodine solution.

The picrates of both morphine and narceine are easily soluble in HCl, acetic acid, and ammonia.

For dissolving morphine picrate about 0·4 gramme of NH_4Cl is required for 0·1 gramme of the alkaloid salt. This solubility is due to dissociation of the compound.

With potassium chromate neutral solutions of narceine give no precipitate at first; but after standing some time one falls, and in from twenty-four to thirty-six hours the separation is quantitative. With morphine under similar conditions only traces of an insoluble compound appear.

Potassium bichromate at first gives no precipitate in neutral narceine solutions. On long standing there is a fine crystalline deposit, which is not quantitative. Morphine under similar conditions exercises a reducing action. There is no deposit in the presence of acid.

Strophantin is almost completely indifferent to most of the usual alkaloid reagents, and its separation is therefore easily effected.

In order to test the applicability of these methods to the separation and estimation of alkaloids in forensic cases, the author mixed weighed quantities of the undermentioned alkaloids with various portions of the dead body, allowed these mixtures to remain for a time until putrefaction had set in, and recovered the alkaloids with the following results:

I.	Taken, 0·1	gramme	narceine	and 0·1	gramme	codeine.
	Found, 0·988	,,	,,	,, 0·0982	,,	,,
II.	Taken, 0·1	,,	strychnine	,, 0·15	,,	veratrine.
	Found, 0·1006	,,	,,	,, 0·1454	,,	,,
III.	Taken, 0·1	,,	morphine	,, 0·1	,,	narceine.
	Found, 0·0932	,,	,,	,, 0·0991	,,	,,

C. A. M.

On the Determination of Formic Acid by Titration with Potassium Permanganate. H. C. Jones. (*Amer. Chem. Jour.*, 1895, xvii., 539-541.)—Péau de Saint-Gilles* was the first to determine formic acid by titration with potassium permanganate in the presence of an alkaline carbonate. Lieben† has confirmed this, using a more elaborate process. The method proposed by the author, and which was worked out in 1891, is on the same principle, but the procedure differs from that of Lieben.

The solution containing the formic acid is made alkaline with Na_2CO_3, warmed, and an *excess* of standard permanganate added. All the formic acid is thus oxidized, and a precipitate of manganese hydroxide thrown down. The solution is acidified

* *Ann. Chim. Phys.*, 1859, lv., 374.

† *Monat. Chem.*, 1893, xiv., 746.

with H_2SO_4, and a measured volume of oxalic acid run in until all the precipitate has dissolved and the permanganate disappeared. The excess of oxalic acid is then titrated with standard permanganate. A volume of oxalic acid equal to that taken is also titrated with the permanganate solution, and the difference between the result and the total permanganate used gives the quantity of permanganate required to oxidize the formic acid. The experimental results quoted agree well among themselves and with those obtained by other methods.

The author further shows that Saint-Gilles' statement that oxalic acid can be titrated in acid solution in the presence of formic acid is unreliable, since formic acid is also oxidized to some extent by the permanganate under these conditions.

C. A. M.

Estimation of Formic Acid. F. Freyer. (*Chem. Zeit.*, 1895, xix., 1184, 1185.)—Scala proposed to heat the neutral solution containing the formic acid with mercuric chloride, and to weigh the precipitated mercurous chloride. The author having occasion to determine the formate in a mixture of calcium acetate and formate, has devised the following method: The mixed calcium salts are distilled with dilute sulphuric acid in a current of steam until the distillate is no longer acid; an aliquot portion of the distillate is titrated with alkali to determine the total acid, whilst another portion is evaporated, if necessary, with excess of caustic soda to concentrate it, and is treated as follows: 10 to 20 c.c., containing about 0·5 gramme of formic acid, are heated for half an hour to an hour with 50 c.c. of a 6 per cent. solution of potassium bichromate and 10 c.c. of concentrated sulphuric acid in a flask provided with an inverted condenser. The liquid is now made up to 200 c.c., and the unaltered chromic acid determined in 10 c.c. of it. For this purpose, 1 to 2 grammes of pure potassium iodide, 10 c.c. of a 25 per cent. solution of phosphoric acid, and some water are added; and after five minutes the solution is diluted to about 100 c.c. with boiled water, and titrated with $\frac{N}{10}$ thiosulphate solution in the usual manner. The phosphoric acid is added according to Meineke's recommendation, and is for the purpose of rendering the change from the blue colour of the iodide of starch to the green of the chromium salt more visible; the commercial glacial acid may be dissolved in water, oxidized by potassium permanganate until it has a faint rose colour, and filtered.

The bichromate solution used for the oxidation is titrated in the same way. One mol. potassium bichromate is equivalent to three mols. formic acid.

The results quoted by the author show that the method is fairly accurate, both in the absence and in presence of acetic acid.

A. G. B.

Interpretation of some Results in the Analysis of Extracts of Fustic. C. S. Boyer. (*Jour. Amer. Chem. Soc.*, 1895, xvii., 518-520.)—The method of analysis employed was as follows: Water was estimated by drying 5 to 6 grammes of the extract in the water-oven until the weight was constant. Two to four grammes of this dry powder were completely exhausted with *absolute* alcohol in a Soxhlet

extractor, and the residue left on distilling the alcohol from the extract dried and weighed. The residue was treated with boiling water and tested for *morin* and *maclurin* (*morin-tannin*) in separate portions, the former by adding a few drops of aluminium sulphate, and the latter by adding ferric chloride. In the samples examined by the author, the result was negative in each case. The residue from the alcoholic extract was ignited in a platinum crucible, and the ash subtracted from the matter soluble in absolute alcohol. The ash percentage was determined on 5 grammes of the powder. The results obtained were:

	I.		II.		III.		IV.		V.	
	Per cent.	On dry basis. Per cent.	Per cent.	On dry basis. Per cent.	Per cent.	On dry basis. Per cent.	Per cent.	On dry basis. Per cent.	Per cent.	On dry basis. Per cent.
Water	67·09	—	50·42	—	36·48	—	49·62	—	6·18	—
Organic matter soluble in absolute alcohol ...	31·34	95·23	38·57	77·79	52·85	83·20	47·41	94·11	75·55	80·53
Ash	0·52	1·58	5·54	11·18	1·24	1·95	1·05	2·08	7·62	8·12
Organic matter insoluble in alcohol	1·05	3·19	5·47	11·03	9·43	14·85	1·92	3·81	10·65	11·36
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The chief mineral constituents of fustic are lime and magnesia, and the amount of these forms one of the guides in determining the method of extraction. The more pressure used the higher, within certain limits, the ash percentage, and the larger the amount of lime and magnesia in the ash. The extracts contained the following quantities of lime and magnesia: I. 41·16 per cent., IV. 46·83 per cent., II. 68·12 per cent., V. 62·15 per cent. of the total ash. The presence of quercitron-bark extract as an adulterant may often be misleading. This was tested for by a series of dye-tests depending on the different affinities of the colouring matter of bark and fustic for alum and tin mordants, but the results were negative.

The conclusions arrived at were that I. was made entirely by the "open extraction" method; II. by the "closed extraction" method, using five to eight pounds pressure; and that III. was extracted in open vessels, but that the change of "waters" was done under pressure. The latter inference was drawn from the fact that the percentage of ash was low, while the "extractive matter" was high; and the only way this could happen would be by opening up the fibre of the wood, as in open boiling, and then applying pressure. The conclusions were subsequently confirmed by experiment.

The origin of the other two samples was known. IV. was made in an open extractor with boiling water. Eight "waters" were taken off, each having remained fifteen minutes in contact with the wood. Sample V. was extracted under five pounds pressure, using seven "waters," and the weak liquor being evaporated to dryness. C. A. M.

A New Method of Analysing Fats and Hydrocarbons. M. Crismer. (*Bull. de l'Assoc. belge des Chimistes*, ix., 1895, pp. 71, 72.)—The method depends on a new physical constant which the author calls the *critical temperature of dissolution*. Several drops of the melted and filtered substance are introduced into a small tube

several millimetres in diameter by means of a capillary pipette. A slightly greater volume of alcohol of known density is then added, and the tube sealed and fixed by a platinum thread to the bulb of a thermometer. It is then heated in a bath of sulphuric acid until the meniscus separating the two layers becomes a horizontal plane. At this point the thermometer is withdrawn from the bath and turned sharply two or three times until the liquid becomes homogeneous, after which it is replaced and the temperature allowed to fall slowly, the thermometer and tube being constantly shaken. The temperature at which a marked turbidity is produced in the liquid is the critical temperature of dissolution.

The conclusions arrived at by the author are: (1) Substances of the same nature have practically the same critical temperature of dissolution. Thus, fourteen butters of guaranteed purity from different sources varied from 98° to 102°, the mean being 100° C.; samples of margarine gave a critical temperature of from 122° to 126°; cocoanut-oil from 71° to 75°; cocoa-butter, 126°; pure beeswax from various sources, 129° to 133°; ozokerite, 175°; Carnauba-wax, 154°; paraffins, according to their constitution and melting-points, 140° to 160°; and essence of terebenthene, 14°.

(2) The critical temperature of a mixture is the arithmetical mean of those of its constituents. C. A. M.

A New Method for the Quantitative Estimation of Starch. M. Dennstedt and F. Voigtländer. (*Forsch. Ber. üb. Lebensm.-Hamburg Chem. Staats Lab.*; through *Chem. Cent.*, 1895, pp. 322, 323.)—According to the authors the blue colour produced by iodine in starch solutions is in direct proportion to the amount of starch, and on this they have based a calorimetric method of estimation. On boiling a little starch in a large quantity of water the starch granulose is in so fine a state of division that it behaves like a solution, while the starch cellulose falls to the bottom. For wheat-starch the relation between them appears to be constant (90·5 : 100). In order to obtain a solution containing a known quantity a pure starch is selected, and the moisture, ash, protein and fat determined and deducted from the amount taken.

A quantity corresponding to 0·5 gramme of starch, as determined by these calculations, is weighed out to the fourth place of decimals, and boiled with a litre of water in a 2-litre flask. On cooling the whole is made up to a litre, the starch cellulose allowed to settle, and 5 c.c. of the supernatant liquid poured into a series of similar cylinders containing 100 c.c. and graduated in $\frac{1}{2}$ c.c.s. One drop of a solution of I in KI is then added to each, and all are made up to 100 c.c. The substance to be examined is treated in the same way, 0·5 gramme being weighed out after the determination of the moisture, etc., and the solution made as in the case of the pure starch. The colour produced by the known solution of starch is then matched by the unknown, and the mean of several determinations taken. As it is more easy to judge a colour between a lighter and a darker, it is advisable to have cylinders, some containing 4·9 c.c. of the known solution and others 5·1 c.c., and to place the one to be examined between them. A constant temperature should be observed, and the solutions always freshly prepared. A violet colour, instead of a blue, may be given with fine meal. This is remedied by stirring the weighed

amount with alcohol, and, after it has stood some time, filtering with the aid of a filter-pump through a starch-free filter. The filter is washed with alcohol, ether, and alcohol again, and is introduced together with the meal into the flask.

C. A. M.

Detection of Naphthol. H. Spinette. (*Bull. de l'Assoc. Belge des Chim.*, ix., 1895, pp. 50-52.)—The use of naphthol as an antiseptic in food products is not of frequent occurrence. The author has only once met with it. This is probably owing to its small solubility in water, and to the taste it communicates. In spite of these drawbacks, however, it may be met with in beverages, and especially in substances sold as preservative agents. It is, therefore, advantageous to determine the best method of isolating and identifying it. Two varieties are known—α-naphthol and β-naphthol. The former crystallizes in colourless needles, fuses at 94°, and boils at 280° C. It has a strong odour of phenol. β-naphthol, or iso-naphthol, forms rhombic colourless crystals, fuses at 122°, and boils at 290°. It is almost without smell, and has a bitter, burning taste. It is but little soluble in water, but dissolves readily in alcohol, ether, chloroform, and solutions of the alkalies.

The detection of the phenols in general has been studied by Desquelle.* In his method the substance to be examined is shaken gently with half its volume of chloroform, the chloroform drawn off by means of a separating funnel, and a small piece of caustic potash added to it. Characteristic colours are obtained, varying with the nature of the phenol.

Phenol	Rose.	Beta-naphthol	Greenish-blue.
Resorcin	Rose.	Pyrogallol	Violet.
Hydroquinone	Golden yellow.	Cresol	Violet.
Alpha-naphthol ...	Sky-blue.	Guaiacol	Violet-rose.

Yvon identifies naphthol by the rose coloration given by it with either of the following reagents:

1. Mercuric nitrate ... ... 5 grammes.
   Nitric acid ... ... 15 ,,
2. Saturated solution of potassium nitrate ... ... 10 ,,
   Sulphuric acid ... ... 5 ,,

The author found that Desquelle's method did not always give conclusive results, and so modified it by making the tests on the residue left on the spontaneous evaporation of the chloroform.

The following test may also be applied: The residue is dissolved in 5 c.c. of caustic soda solution, and an aqueous solution of 0·05 gramme of aniline sulphonic acid added. This is made by dissolving the acid in 5 c.c. of normal soda solution, and then adding 5 c.c. of normal H_2SO_4 and 0·02 gramme of sodium nitrite.

With alpha-naphthol a blood-red colour is obtained; with beta-naphthol a yellowish red.

C. A. M.

A New Method of estimating Indigotin. Josef Schneider. (*Zeit. Anal. Chem.*, 1895; *Drittes Heft.*, pp. 347-354.)—All the methods in use for estimating indigotin are more or less unsatisfactory, especially when used to determine it in

* *Repertoire de Pharmacie*, 1890, p. 101.

coloured fabrics. The errors in most of them were pointed out by Von Cochenhausen,* while Ulzer† in turn showed that the process of Von Cochenhausen and Hönig was very liable to error, since on continued boiling with aniline a considerable amount of indigo was lost, for which no correction was possible. The author considered the method of W. Stein‡ as being the most promising. In this 0·2 gramme of indigo is boiled for fifteen minutes with 20 c.c. of an animal oil with a boiling-point above 180° C. The liquid is poured on to a filter, and the boiling repeated with 10 c.c. of oil (at least three times), until the indigotin is completely extracted. The cooled filtrate is then well shaken with twice its volume of ether, allowed to stand for an hour, filtered through a weighed filter, the deposit washed with ether, dried at 100°, and weighed.

According to the author, there are three main objections to this process.

1. Indigo only dissolves in considerable quantities at the boiling temperature of the oils, and only in those which boil above 180°. As the temperature falls, the solubility declines very rapidly. It is, therefore, necessary to filter at a high temperature.

2. Indigotin cannot be completely precipitated from its solution in animal oils.

3. As in the case of aniline extraction, there is a loss of indigo on heating with animal oils, this being greater the more oil and indigo are used, and the longer the boiling is continued.

The principal novelties in the author's process are the use of a special extraction apparatus and of a solvent (naphthalene) which does not act on indigotin.

The naphthalene (50 grammes) is boiled in an Erlenmeyer flask, through the cork of which passes a tube 15 millimetres in width and a metre long. In the side of the tube within the flask there is an opening, and the bottom of the tube is contracted and slightly bent. The indigo ($\frac{1}{2}$ to 1 gramme) is mixed with glass wool, placed in a paper coil surrounded by a linen one, and suspended below the bottom of the tube in the flask, so that the naphthalene falls into the coil. In order that accurate results may be obtained, the naphthalene must be free from ash. The boiling must be continued until the drops falling from the coil are quite colourless. On cooling, the naphthalene solution of indigotin is decomposed with ether, filtered, and weighed, as in Stein's method. The correction to be applied for the indigo decomposed and remaining in solution depends on the relative quantities of naphthalene and indigo used, on the duration of the extraction (with 1 gramme of indigo usually $5\frac{1}{2}$ hours), on the manner of heating, and on the possibility of overheating. In order to determine it, the indigotin obtained on the filter should again be extracted with naphthalene under exactly similar conditions, and the loss on again weighing the indigotin gives the necessary correction. With 50 grammes of commercial white naphthalene which was not quite pure, the loss of indigotin on heating over wire gauze was 1 to 4 milligrammes, corresponding to a correction of +0·1 to 0·4 per cent., with 1 gramme of indigo. By using purified naphthalene and heating on an oil bath, the loss would certainly have been less.

* *Leipziger Monatshefte für Textil industrie*, 1888.
† *Mitth. des technol. Gewerb.*, Vienna, 1891.
‡ *Die Prüfung der Zeugfarben und Farb materialen*, 1874.

Care must be taken to have the apparatus and the indigo completely dry, in order to avoid the risk of explosions. C. A. M.

Amalgamated Aluminium as a Neutral Reducing Agent in Presence of Water. H. Wislicenus and L. Kaufmann. (*Ber.*, 1895, xxviii., 1323.)—An amalgam of aluminium containing as little as one atom of mercury to forty-five of aluminium decomposes water with greater energy than the well-known amalgam of sodium, while the mercury serves only as a "catalytic" agent. On alcohol and ether it has no action, and may be used, therefore, to remove every trace of moisture from these bodies. Although the evolution of hydrogen is somewhat stormy, the action can be perfectly regulated by cooling the liquid. As a reducing agent, the substance to be treated is dissolved in ether or absolute alcohol (aqueous alcohol or even water may be used if necessary), an excess of the amalgam added, and water dropped in with constant agitation. The action is usually complete in a very short time, and the alumina may be filtered off or removed by the pump, and will rarely be found to retain any of the organic substance. Any other indifferent solvent or mixture of solvents may be employed so long as they dissolve traces of water.

The amalgam is prepared by treating aluminium turnings (freed from oil) with caustic soda until they are attacked. They are rinsed in water, and a 0·5 per cent. solution of mercuric chloride allowed to act for one or two minutes. The operations are repeated, and the black amalgam is washed rapidly in water, alcohol, and ether, and preserved, if necessary, under petroleum spirit. This process is specially adapted to the reduction of nitro-compounds. Its use on a commercial scale is the subject of a patent. F. H. L.

The Action of Thiacetic Acid on Various Metallic Solutions in the Cold. N. Tarugi. (*Gazz. Chim. Ital.*, 1895, xxv. [I.], 341; through *Chem. Zeit. Rep.*, 1895, 201.)—When employing thiacetic acid to replace sulphuretted hydrogen in ordinary analysis, it is necessary to conduct the precipitation in hot solutions, in which case only are pure sulphides thrown down. By adding this reagent to cold neutral mercuric chloride solution, washing and drying the precipitate in the dark, extracting with carbon disulphide, and finally drying over sulphuric acid *in vacuo*, a white thio-chloride ($2HgS,HgCl_2$) is obtained, soluble only in aqua regia. A similar thio-nitrate may be prepared, which is blackened by caustic soda or ammonia. The white precipitate obtained from an aqueous mercuric acetate solution could not be analysed owing to its instability, but by employing an alcoholic solution of the same salt a white crystalline powder turning to yellow was obtained, consisting of a mixture of normal and basic mercuric thiacetate separable by boiling chloroform, in which only the neutral salt is soluble. On cooling, this is thrown down as white, mother-of-pearl-like crystals, which, when pure, are unchanged by light and air, and are soluble in warm petroleum spirit, less so in alcohol and carbon disulphide. It is unchanged by boiling water or by dilute cold hydrochloric acid, but warm dilute hydrochloric or cold dilute sulphuric acid converts it into the previously described thio-chloride. The basic mercuric thiacetate is an amorphous orange powder in-

soluble in hydrochloric or nitric acid and ammonium sulphide, but dissolved by aqua regia.

Cold neutral copper sulphate yields a green precipitate, probably a mixture of sulphide and thiacetate. Cadmium solutions give a white amorphous precipitate of thiacetate, which, when moist, is altered by exposure to light, is soluble in warm dilute acids, and by the addition of ammonia or ammonium sulphide or boiling with water is changed into the sulphide. Lead solutions also yield a mixture of thiacetate and sulphide, the former being soluble in boiling water, and forming white needles permanent in light and insoluble in alcohol, chloroform, and petroleum spirit. Nitric acid converts it into lead sulphate; ammonia, caustic soda, and ammonium sulphide into lead sulphide. Silver salts give a reddish precipitate with this reagent, but it is too unstable to allow of analysis.

For the preparation of thiacetic acid for use in chemico-legal investigations, R. Schiff (*Ber.*, 1895, xxviii., 1204) recommends 300 grammes of phosphorus pentasulphide, 150 grammes of broken glass, and 300 grammes of glacial acetic acid to be gently warmed together in a 2-litre flask fitted with a thermometer and an inverted condenser. When the vapours reach 103° the operation is stopped and the product rectified several times, the portion distilling between 92°-97° being kept. Prepared as above, the reagent is absolutely free from arsenic. F. H. L.

A New Method for the Separation of Copper and Cadmium in Qualitative Analysis. A. S. Cushman. (*Amer. Chem. Jour.*, 1895, xvii., 379-383.)—It is well known that cadmium combines with the chlorides of the metals of the alkalies and alkaline earths, forming, according to Hauer, compounds of the general formulæ $4RCl,CdCl_2$; $2RCl,CdCl_2$; $RCl,CdCl_2$. With ammonium chloride the compound $2NH_4Cl,2CdCl_2,H_2O$ has been obtained. These double chlorides are formed when cadmium sulphide is treated with dilute hydrochloric acid in the presence of alkaline chlorides, the reaction being $CdS + 2RCl + 2HCl = CdCl_2,2RCl + H_2S$. This property of cadmium sulphide is used by the author as the principle of a delicate test for cadmium. If to 2 c.c. of a solution containing a small amount of cadmium, 10 c.c. of a saturated solution of NaCl and a few drops of dilute hydrochloric acid be added, hydrogen sulphide produces no precipitate even when passed in to saturation. If a few drops of dilute ammonia be allowed to run down the side of the tube, a yellow ring forms at the junction of the liquids. This test was sensitive with a solution containing less than 0·01 milligramme of cadmium, a perceptible ring appearing after standing half an hour.

In separating the sulphides of copper and cadmium, the latter entirely dissolves on adding a strong solution of salt and a little hydrochloric acid. On diluting the filtrate and adding hydrogen sulphide, the cadmium is re-precipitated. Care must be taken that lead and bismuth are absent, since the sulphides of these metals are also soluble in strong acidified solutions of the alkaline chlorides. C. A. M.

The Estimation of Citrate-soluble Phosphoric Acid in Thomas' Slag. P. Wagner. (*Chem. Zeit.*, 1895, xix., 1419.)—When this process was first devised it was intended only as a rough test for different makes of slag, and to serve as a means of detecting adulteration. The material was then of very irregular composition, and samples, all containing about the same amount of total phosphoric acid, differed very widely in their solubility in ammonium citrate solution, and consequent manurial value. The position has now changed. The manufacture of the slag has been greatly improved, and the process of examination has proved itself so exact, that it has been adopted in Germany as the standard method for the commercial valuation of basic slag. It is important, however, in carrying out the process to adhere strictly to all the details mentioned, as any departure from the regular routine in strength or temperature of solutions, or time of digestion, etc., may be followed by grave errors.

Strong Ammonium Citrate.—1,500 grammes of pure crystallized citric acid are dissolved in about 2 litres of water, 3½ litres of 8 per cent. ammonia added, and, when cold, the liquid is made up to 8 litres. In a small quantity (2·5 c.c.) of this solution the ammonia is determined by distillation with magnesia, and, finally, enough ammonia and water are added to the bulk to make 10 litres of solution, containing exactly 279·3 grammes of ammonia. A *dilute citrate solution* is prepared by mixing two volumes of this solution with three volumes of water.

Molybdate Solution.—Prepared either by dissolving 150 grammes of ammonium molybdate in water, or 125 grammes of molybdic acid in 100 c.c. of water and 300 c.c. of 8 per cent. ammonia. Four hundred grammes of ammonium nitrate are added, the solution made up to one litre, and poured into an equal volume of nitric acid (specific gravity 1·19). After standing twenty-four hours at 35°C., the whole is filtered.

Magnesia Mixture.—110 grammes of pure magnesium chloride and 140 grammes of ammonium chloride are dissolved in 700 c.c. of 8 per cent. ammonia and 1,300 c.c. of water, the solution being filtered after standing several days.

Five grammes of the slag just as received are put into a half-litre bottle and filled up to the mark with the dilute citrate solution at a temperature of 17½° C.; a rubber cork is inserted in the neck, and the bottle shaken mechanically for half an hour (if a revolving apparatus be employed, the speed should be thirty to forty revolutions per minute). The liquid is then immediately filtered as rapidly as possible, the filtrate being returned to the filter if not clear. Fifty c.c. are measured into a beaker, 100 c.c. of the molybdate solution added, and placed for ten to fifteen minutes in a water-bath at 80° to 95°. When cold, the precipitate is filtered off, washed with 1 per cent. nitric acid, and dissolved in 100 c.c. of cold 2 per cent. ammonia (should this solution not be perfectly clear, the analysis is useless). Fifteen c.c. of the magnesia mixture are next added drop by drop, with constant stirring, the vessel covered over and put aside for two hours; the precipitate is then filtered, washed with 2 per cent. ammonia, and ignited as usual. The temperature of agitation (17½° C.) is specially important, and must be maintained as accurately as possible during the whole of the thirty minutes. F. H. L.

CORRESPONDENCE.

To the Editors of THE ANALYST.

SIRS,—In reply to Dr. E. Frankland's letter in this month's ANALYST, permit me to say that I had not seen the Registrar-General's annual summary referred to, and, therefore, was not aware that Dr. Frankland had suggested a specific cause for the discrepancies in question. The suggestion does not appear to be quite satisfactory, because the companies' chemist's organic C is very frequently about twice as much as Dr. Frankland's, whereas, if the suggested cause of the discrepancies in the N is the true one, it should be less. It is, however, remarkable that such an error could have been allowed to exist for so long a time without rectification.

I may mention that I brought the matter of these differences in analytical results before the Royal Commission on Metropolitan Water Supply, 1892, and handed in a statement, a copy of which I enclose. I also discussed the subject in a paper contributed to the Sanitary Congress at Portsmouth in 1892, a copy of which is also enclosed. Dr. E. Frankland's statement refers only to the results obtained by the chemists acting for seven of the London Water Companies. The chemist for the other company—the Kent—was the late Dr. A. Bernays, and I know from personal experience that he strictly adhered to all the directions given by Dr. Frankland in his book.

In my paper I give the results obtained by the late Dr. Bernays during 1891, and the differences between these and Dr. E. Frankland's are enormous, and far exceed those of any of the others.

Since February, this year, the results of an analysis of the Kent company's water by Dr. P. Frankland have been published in the monthly reports of the official water examiner. The organic C and N figures in these analyses differ vastly from those obtained by Dr. E. Frankland from the same company's water, as will be seen below :

		Dr. P. Frankland.	Dr. E. Frankland.
February... ...	Organic C	·0557 ...	... ·04
„	„ N	·0157 ...	. . ·005
March	„ C	·0557 ...	... ·038
„	„ N	·0157 ...	... ·005
April	„ C	·0485 ...	... ·023
„	„ N	·01 ...	... ·005
May	„ C	·0485 ...	... ·024
„	„ N	·0157 ...	... ·008
June	„ C	·0471 ...	... ·024
„	„ N	·0114 ...	... ·006

It is curious that the N in Dr. P. Frankland's results for February and March should be three times, and in April, May, and June twice as much as Dr. E. Frankland obtained.

There are many other discrepancies to be found in the published results of the analyses by the companies' chemists as compared with Dr. E. Frankland's, since they have added the "inch of copper oxide in front" to the contents of the combustion-tube ; but I think the above are sufficient to show that the process does not in practice give reliable results even in the hands of the most experienced operators.—I am, sir, your obedient servant,

W. C. YOUNG.

LONDON, *August* 23, 1895.